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DESCRIPTION

TERNARY METAL COLLOID HAVING THREE LAYER CORE/SHELL  
STRUCTURE AND PROCESS FOR PRODUCING THE TERNARY METAL  
5 COLLOID

TECHNICAL FIELD

The present invention relates to a ternary metal colloid having a three layer core/shell structure and a process for producing the ternary metal  
10 colloid.

BACKGROUND ART

In recent years, the application of metal colloids to the manufacture of materials in various fields, such as catalysts, and optical, electrical, and  
15 magnetic materials, has been studied. A metal colloid means a state in which fine particles (nanoparticles) of metals, ceramics, etc. having a particle size of 1 to 100 nm, which are insoluble in a solvent, are dispersed and suspended in a solvent, and a colloid solution using a liquid as the solvent is generally known. The nanoparticle means an atom group in the order of  
20 nanometers composed of two, three, or more atoms, not of a single atom.

In order to use a metal colloid to produce various materials, usually, the metal colloid is impregnated into a suitable support medium to adsorb nanoparticles. For example, in the case of production of a catalyst, a porous material (carbon fine powder, alumina powder, etc.) called a carrier is used as  
25 the support medium, and a metal colloid is adsorbed onto the carrier, whereby the catalyst is produced. It is conceivable that the catalyst in which nanoparticles are carried by using the metal colloid exhibits a reaction behavior different from that of a general catalyst in which an atomic or

molecular metal is carried. It is anticipated that future studies will discover the catalyst using a colloid has superior properties.

Some catalysts and optical, electrical, and magnetic materials are produced by adsorbing a plurality of kinds of metal nanoparticles, not one 5 metal nanoparticles. The reason why a plurality of metal nanoparticles are adsorbed is that a synergistic effect of the adsorbed metal nanoparticles is achieved, and thereby the intended performance can be offered more effectively.

In the case where a plurality of kinds of metal nanoparticles are 10 adsorbed, it is deemed better to adsorb the metal nanoparticles in a state wherein different metal nanoparticles are close to each other. Therefore, a metal colloid for adsorbing the plurality of kinds of metal nanoparticles that are close to each other has been studied. However, the conventional study examples mainly relate to a binary metal colloid for adsorbing two metal 15 nanoparticles (the conventional arts relating to the binary metal colloid are disclosed in, for example, the following Patent Documents).

Patent Document 1: Japanese Patent Laid-Open No. 2000-279818

Patent Document 2: Japanese Patent Laid-Open No. 2000-279824

If the adsorbed metal is increased in terms of variety though there will 20 be a limit, it is predicted that the properties of the produced material are also enhanced. Therefore, the present invention provides a ternary metal colloid and a process for producing the same, in which three metal atoms can be arranged in design in a good arrangement state.

## 25 DISCLOSURE OF THE INVENTION

The inventors conducted studies earnestly, and found out a metal colloid comprising metal nanoparticles which is composed of metal particles

of three kinds and has a particular structure, thus arriving at the present invention.

Specifically, the present invention provides a ternary metal colloid comprising metal nanoparticles which is composed of three different metal 5 elements and has a three layer core/shell structure.

The three layer core/shell structure means a laminar structure in which metal particles of three kinds are not mixed into one phase, but metallic particles of one kind are covered with metallic particles of other kinds. The nanoparticles having the three layer core/shell structure keep the structure in 10 an intact state even if they are adsorbed onto a support medium. Also, even if the support medium after adsorption is subjected to heat treatment, the nanoparticles do not decompose, and the metal particles constituting the nanoparticles keep their state of being close to each other. Therefore, according to the present invention, three metals can be adsorbed and fixed in 15 a good state in which they are close to each other, and thereby various materials including catalysts having excellent properties can be produced.

In the metal colloid according to the present invention, the metal nanoparticles are preferably protected by a compound called a protective agent. The protective agent means a compound that is chemically or 20 physically bonded to around the nanoparticles in the metal colloid and is adsorbed to restrain the aggregation of nanoparticles and to control and stabilize the particle size distribution to a proper range. By adding the protective agent, the state in which the nanoparticles having a small particle size is suspended is maintained, and in manufacturing a catalyst, the particle 25 size of catalyst particle is decreased, and hence the effective surface area can be made as large as possible. As the protective agent, a chemical species of high molecular weight and low molecular weight which interacts with the metal nanoparticles and is soluble in a solvent is used. Specifically,

poly(N-vinyl-2-pyrrolidone), poly(sodium acrylate), polyethylene glycol, a copolymer containing these compounds, or the like is preferably used.

The metal element constituting the nanoparticles is not subject to any special restriction, but considering the application of the metal colloid

5 according to the present invention, platinum, palladium, silver, gold, ruthenium, rhodium, iridium, and osmium are cited as a favorable metal element.

According to the inventors, as a process for producing the metal colloid having a three layer core/shell structure according to the present invention,

10 some processes can be used. First, a first process is to mix metal colloid comprising metal nanoparticles which is composed of two metal elements and has a core/shell structure with a metal colloid comprising metal nanoparticles which is composed of a metal element different from the aforementioned two metal elements. A phenomenon that by merely mixing the two metal colloids

15 in this manner, metal nanoparticles of one kind is arranged so as to surround metal nanoparticles of the other kind is an unexpected one, but has been confirmed by the verification of the inventors.

The steps of the first production process is explained in detail. The first production process includes a step of producing a first metal salt solution

20 in which two metal ions are dispersed by dissolving two metal salts into a first solvent, and producing a first colloid solution comprising metal nanoparticles which is composed of two metal elements and has a core/shell structure by reducing the two metal ions in the first metal salt solution; a step of producing a second colloid solution as nanoparticles by dissolving one metal salt

25 different from the two metal salts into a second solvent and by reducing the one metal ion; and a step of mixing the first colloid solution with the second colloid solution.

The metal colloid according to the present invention is preferably protected by a protective agent. This protective agent is preferably added together with the metal salts when the first and second colloid solutions are produced. As the protective agent to be added, poly(N-vinyl-2-pyrrolidone),  
5 poly(sodium acrylate), polyethylene glycol, a copolymer containing these compounds, or the like is preferably used.

Also, when the first and second colloid solutions are produced, the metal ions are preferably reduced by the addition of a reducing agent. To reduce a noble metal salt in the solution, a method in which the noble metal  
10 salt is reduced electrochemically by inserting an electrode into the solution to perform energization can also be used. However, the method in which a reducing agent is added enables homogeneous reduction. Also, in the case of electrochemical reduction, a power source, electrode, and control unit for reducing the solution are required, and the equipment configuration for  
15 producing colloid solution is complicated. Also, it is difficult to set the current, voltage, and other conditions for performing reduction properly. As the reducing agent, any of an inorganic or organic compound of gas, liquid, or solid, or physical energy, which has a force for reducing metal ions, can be used. Specifically, hydrogen, hydrazine, sodium borohydride ( $\text{NaBH}_4$ ),  
20 alcohols such as ethanol and methanol, citric acid, N-methylpyrrolidone, dimethylformamide, diethylaminoboron, formaldehyde, light (visible rays, ultraviolet rays), gamma rays, ultrasonic waves, and the like can be used.

In the case where the protective agent can perform a reducing action, the colloid can be produced by mixing the metal salt with the protective agent  
25 by means of a solvent without the addition of a reducing agent. Also, as the solvent, water, methanol, tetrahydrofuran, acetone, and the like can be used. In the case where a solvent that can perform a reducing action is used, the colloid can be produced without an addition of a reducing agent.

A mixing ratio between the first colloid solution and the second colloid solution exerts an influence on the quantity of metal arranged in the outermost layer of metal nanoparticles, and also exerts an influence on the properties thereof. If the mixed quantity of second colloid solution is too small, the 5 colloid is substantially no different from the colloid having a two layer structure. The mixing ratio between the two solutions changes according to the composition of metal elements constituting the first colloid solution. The mixing ratio (first colloid solution:second colloid solution, metal atom ratio) is preferably 1:0.5 to 1:50, far preferably 1:2 to 1:15.

10 A second production process for the metal colloid according to the present invention basically involves producing a unitary or binary metal colloid is produced, and providing the metal nanoparticles in the metal colloid with an activity as a reduction catalyst. Specifically, in the case of using the former unitary metal colloid, after a unitary metal colloid is produced, and the metal 15 nanoparticles in the metal colloid are provided with an activity as a reduction catalyst, this metal colloid is mixed with a metal salt solution to produce a binary metallic colloid, and further the metal colloid in which the nanoparticles in the binary metal colloid are provided with an activity as a reduction catalyst is mixed with a metal salt solution to form a ternary metal colloid. In the case 20 of using the latter binary metal colloid, after a binary metal colloid is produced, and the metal nanoparticles in the metal colloid are provided with an activity as a reduction catalyst, this metal colloid is mixed with a metal salt solution to form a ternary metallic collide. In these cases, since the activity as a reduction catalyst of metal nanoparticles is utilized, the metal ions are easily 25 reduced on the surface of metal nanoparticles, and hence metal nanoparticles of a desired form can be formed.

The step of the second production process is explained in detail. The second production process includes a step of producing a solution in which

first metal ions are dispersed in a solvent by dissolving a first metal salt into a first solvent, and producing a first colloid solution by reducing the first metal ions; a step of providing first metal nanoparticles in the first colloid solution with an activity as a reduction catalyst; a step of producing a second metal 5 salt solution by dissolving a second metal salt into a second solvent, and mixing the first metal nanoparticles with the second metal salt solution and reducing second metal ions to form a binary colloid solution; a step of providing second metal nanoparticles in the binary colloid solution with an activity as a reduction catalyst; and a step of producing a third metal salt 10 solution by dissolving a third metal salt into a third solvent, and mixing the second metal nanoparticles with the third metal salt solution and reducing third metal ions.

Also, the second production process includes a step of producing a first metal salt solution in which two metal ions are dispersed in a solvent by 15 dissolving two metal salts into a first solvent, and producing a colloid solution comprising metal nanoparticles which is composed of two metal elements and has a core/shell structure by reducing the two metal ions in the first metal salt solution; a step of providing the metal nanoparticles in the first colloid solution with an activity as a reduction catalyst; and a step of producing a second 20 metal salt solution by dissolving one metal salt different from the two metal salts into a second solvent, and mixing the metal nanoparticles with the second metal salt solution and reducing metal ions in the second metal salt solution.

In the step of providing the nanoparticles in the produced colloid 25 solution with an activity as a reduction catalyst, in addition to a method in which the nanoparticles are treated by hydrogen molecules, whereby hydrogen is adsorbed onto the surface of nanoparticles, a method in which metal nanoparticles are treated by a reducing chemical species or a reducing

agent is used. With this method as well, when a metal colloid is produced, a protective agent and a reducing agent are preferably used. The details thereof are the same as those in the first production process.

A third production process according to the present invention is what is 5 called a simultaneous reduction process, in which a metal salt solution in which three metal ions are dispersed in a solvent is produced by dissolving three different metal salts into a solvent, and the three metal ions are reduced.

With the third production process as well, a protective agent is preferably added, and to reduce metal ions, a reducing agent is preferably 10 added. The details thereof are the same as those in the first and second production processes.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an FT-IR spectrum of a unitary metal colloid composed of 15 platinum, palladium, or rhodium;

Fig. 2 is an FT-IR spectrum of a binary metal colloid composed of platinum and palladium; and

Fig. 3 is an FT-IR spectrum of a ternary metal colloid composed of platinum, palladium, and rhodium.

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#### BEST MODE FOR CARRYING OUT THE INVENTION

Preferred embodiments of the present invention will now be described together with comparative examples.

First embodiment: In a first embodiment, a binary metal colloid composed of 25 platinum and palladium and a unitary metal colloid composed of rhodium were produced, and the two colloids were mixed with each other to produce a ternary metal colloid composed of platinum, palladium, and rhodium.

Production of binary metal colloid composed of platinum and palladium:

PVP weighing 0.5868 g (0.66 mmol: R = 40) was extracted, and was agitated in a nitrogen atmosphere for 15 minutes after 92 cm<sup>3</sup> of water was added.

After agitation, 1.6 cm<sup>3</sup> of hexachloroplatinic (IV) acid (H<sub>2</sub>[PtCl<sub>6</sub>]<sub>6</sub>) aqueous

5 solution and 6.4 cm<sup>3</sup> of palladium chloride (PdCl<sub>2</sub>) aqueous solution of 0.0166 M were added to the PVP solution, and the solution was agitated for 30 minutes. To this agitated solution, 100 cm<sup>3</sup> of ethanol was added as a reducing agent so that the water-to-ethanol ratio should be 1:1. Refluxing by heating was performed for 2 hours, whereby a PVP-protected binary metal

10 colloid composed of platinum and palladium was obtained.

Production of unitary metal colloid: PVP weighing 0.5868 g (0.66 mmol: R = 40) was extracted, and was agitated in a nitrogen atmosphere for 15 minutes after 96.6 cm<sup>3</sup> of water was added. After agitation, 3.4 cm<sup>3</sup> of rhodium

chloride (III) (RhCl<sub>3</sub>) aqueous solution of 0.0166 M was added to the PVP

15 solution, and the solution was agitated for 30 minutes. To this agitated solution, 100 cm<sup>3</sup> of ethanol was added as a reducing agent so that the water-to-ethanol ratio should be 1:1. Refluxing by heating was performed for 2 hours, whereby a PVP-protected unitary metal colloid composed of rhodium was obtained.

20 Production of ternary metal colloid composed of platinum, palladium, and rhodium: The PVP-protected binary metal colloid composed of platinum and palladium (0.66 mM, water:ethanol = 1:1) and the PVP-protected unitary metal colloid composed of rhodium (0.66 mM, water:ethanol = 1:1), which were produced as described above, were physically mixed with each other at

25 room temperature. Thereby, rhodium nanoparticles were arranged on the palladium surface of platinum/palladium nanoparticle in the binary metal colloid composed of platinum and palladium, whereby a ternary metal colloid composed of platinum, palladium, and rhodium could be produced.

Verification of particle structure: The particle structure of the ternary metal colloid composed of platinum, palladium, and rhodium, which was produced as described above, was investigated. This investigation was carried out with the use of an FT-IR spectrum, and the particle structure was determined

5 from a change in absorption spectrum at the time when carbon monoxide was adsorbed onto the ternary colloid. Samples for IR analysis were prepared as described below. After the solvent of each colloid solution was distilled off, the colloid solution was dried under reduced pressure at 40°C. Thereafter, the dried colloid was dispersed in dichloromethane. A half of fluid dispersion

10 was put into a Schlenk tube of 50 mL to perform freeze-dearing, and was exposed to a carbon monoxide atmosphere. After the operation of freeze-dearing and exposure to carbon monoxide atmosphere was repeated three times, the solution was agitated further in a carbon monoxide atmosphere for 1 hour, whereby a sample was prepared.

15 The results of this investigation are shown in Figs. 1 to 3. Fig. 1 shows absorption spectra of unitary metal colloid composed of platinum and unitary metal colloid composed of palladium, which were produced for this investigation, in addition to the aforementioned unitary metal colloid composed of rhodium. From these spectra, in the unitary metal colloid

20 composed of platinum, a strong linear absorption peak was observed near a wave number of  $2065\text{ cm}^{-1}$ , and a weak bridging peak was observed near a wave number of  $1868\text{ cm}^{-1}$ . Also, in the unitary metal colloid composed of palladium, strong peaks were observed near wave numbers of  $2044\text{ cm}^{-1}$  and  $1924\text{ cm}^{-1}$ . Further, in the unitary metal colloid composed of rhodium, peaks

25 were observed near wave numbers of  $2065\text{ cm}^{-1}$ ,  $2026\text{ cm}^{-1}$ ,  $1990\text{ cm}^{-1}$ , and  $1891\text{ cm}^{-1}$ .

Fig. 2 shows an absorption spectrum at the time when carbon monoxide is adsorbed onto a binary metal colloid composed of platinum and

palladium. According to this spectrum, a strong peak that seems to be resulted from palladium was observed near a wave number of 1924 cm<sup>-1</sup>. From this result, it was recognized that the particles constituting the binary colloid have a core/shell structure in which platinum is covered with palladium.

5 Fig. 3 shows absorption spectra at the time when carbon monoxide is adsorbed onto ternary colloids produced in this embodiment. From Fig. 3, regarding the adsorption peak of ternary colloid, a peak (near 1924 cm<sup>-1</sup>) inherent in palladium disappears due to the addition of unitary metal colloid composed of rhodium, and peaks inherent in rhodium are formed near wave 10 numbers of 2065 cm<sup>-1</sup>, 2026 cm<sup>-1</sup>, 1990 cm<sup>-1</sup>, and 1891 cm<sup>-1</sup>. That is to say, the nanoparticles in this colloid have a three layer core/shell structure the outermost layer of which is composed of rhodium. Also, this tendency becomes remarkable as the mixing ratio of rhodium colloid increases.

Evaluation of catalytic activity: A catalyst was adjusted by using the ternary 15 colloid produced in this embodiment, whereby the catalytic activity was evaluated. The catalyst was produced by diluting the produced metal colloid solution with a volume of 0.3 mL with 18.7 mL of ethanol, and by agitating the solution at 30°C and 1 atm in a hydrogen atmosphere for 30 minutes to several hours in a form of fluid dispersion of catalyst until hydrogen is not 20 absorbed. Also, the catalytic activity was evaluated by subjecting the fluid dispersion of catalyst to hydrogenation reaction of methyl acrylate and by investigating the hydrogenated catalytic activity at this time. More specifically, in a hydrogenating apparatus, 1 mL of ethanol solution of 0.5 mol/L of methyl acrylate was added to the aforementioned fluid dispersion of 25 catalyst with a volume of 19 mL as a substrate to make the metal mol concentration in ethanol 10 µmol/L, and the reaction was carried out at normal pressure. The measurement was continued until the hydrogenation reaction ended. The hydrogenating catalytic activity was evaluated as described

below. A consumption of hydrogen gas was measured in the hydrogenation reaction and the measurement results were plotted on a graph, the initial rate was determined by the least-square method, and what mol of hydrogen molecules had been consumed per unit time by 1 mol of metal was calculated.

5 The result is given in Table 1. For comparison, Table 1 also gives the investigation results of catalysts prepared by binary and unitary colloids.

[Table 1]

	Hydrogenating catalytic activity (mol-H <sub>2</sub> ·mol·M <sup>-1</sup> ·s <sup>-1</sup> )
Pt/Pd/Rh ternary colloid	22.5
Pt/Pd binary colloid	14.0
Pt unitary colloid	1.3
Pd unitary colloid	7.8
Rh unitary colloid	8.8

From Table 1, it was verified that the catalyst prepared by the ternary

10 colloid in accordance with this embodiment has a highest catalytic activity among the catalysts having been evaluated in this investigation, the catalytic activity being about 2.5 to 17 times of that of unitary colloid, and about 1.5 times of that of binary colloid.

Also, the activity per unit surface area was calculated, and the following

15 calculation result was obtained.

[Table 2]

	Hydrogenating catalytic activity (mol-H <sub>2</sub> ·m·M <sup>-2</sup> ·s <sup>-1</sup> )
Pt/Pd/Rh ternary colloid	23.7
Pt/Pd binary colloid	14.7
Pt unitary colloid	1.2
Pd unitary colloid	8.0
Rh unitary colloid	8.5

As seen from Table 2, it was verified that the catalyst produced based on the ternary colloid produced in this embodiment has a highest activity, and exhibits a high activity without depending on the particle size.

Second embodiment: In a second embodiment, a ternary metal colloid was

5 produced by the second production process of this patent application, namely, by mixing a binary metal colloid having an activity as a reduction catalyst with a metal salt solution. PVP weighing 2.9340 g was extracted, and was agitated for 20 minutes after 100 cm<sup>3</sup> of ethylene glycol was added. Then, 7.2 cm<sup>3</sup> of hexachloroplatinic (IV) acid aqueous solution of 0.0166 M was  
10 added to the PVP solution to adjust the pH value to 10. In a nitrogen atmosphere, refluxing by heating was performed at 190°C for 3 hours. Thereafter, the solution was filtrated with an ultrafilter, and was vacuum dried at 40°C.

The platinum nanoparticles extracted by the above-described method  
15 were dispersed in 150 cm<sup>3</sup> of mixed solution of water, ethanol, and ethylene glycol (water:ethanol:ethylene glycol = 1:1:1), and hydrogen was adsorbed onto the nanoparticles in a hydrogen atmosphere. Then, 100 cm<sup>3</sup> solution of palladium chloride of 0.0166 M was dripped by taking time of 4 to 6 hours, and after dripping, the mixed solution was agitated for 8 hours. Thereafter, the  
20 solution was filtrated with an ultrafilter, and was vacuum dried at 40°C, whereby Pt/Pd binary nanoparticles were obtained.

After the Pt/Pd binary nanoparticles were dispersed in 150 cm<sup>3</sup> of mixed solution of water, ethanol, and ethylene glycol like the mixed solution described above, hydrogen was adsorbed onto the nanoparticles in a  
25 hydrogen atmosphere. Further, 100 cm<sup>3</sup> of rhodium chloride of 0.0386 M was dripped by taking time of 4 to 6 hours, and after dripping, the mixed solution was agitated for 8 hours. Thereafter, the solution was filtrated with an ultrafilter, and was vacuum dried at 40°C. Finally, water and ethanol were

added to the dried powder so that the mixing ratio should be 1:1, whereby a ternary colloid solution containing platinum, palladium, and rhodium was obtained.

Third embodiment: In a third embodiment, a ternary metal colloid was 5 produced by the third production process of this patent application, namely, the simultaneous reduction process. PVP weighing 0.5868 g (0.66 mmol: R = 40) was extracted, and was agitated in a nitrogen atmosphere for 15 minutes after 92.5 cm<sup>3</sup> of water was added. After agitation, 5.8 cm<sup>3</sup> of hexachloroplatinic (IV) acid aqueous solution, 1.4 cm<sup>3</sup> of palladium chloride 10 aqueous solution, and 0.3 cm<sup>3</sup> of rhodium chloride aqueous solution of 0.0166 M were added to the PVP solution, and the solution was agitated for 30 minutes. To this agitated solution, 100 cm<sup>3</sup> of ethanol was added as a reducing agent so that the water-to-ethanol ratio should be 1:1. Refluxing by heating was performed for 2 hours, whereby a PVP-protected ternary metal 15 colloid composed of platinum, palladium, and rhodium was obtained.

For the ternary metal colloid composed of platinum, palladium, and rhodium produced in the above-described second and third embodiments, the structure of nanoparticles in the colloid was investigated with the use of an FT-IR spectrum as in the case of the first embodiment. As a result, almost 20 the same result as that of the first embodiment was obtained, but the catalytic activity was slightly lower than that in the first embodiment.